

- 19) Japanese Patent Agency (JP)
12) official bulletin of publicly disclosed patents (A)
11) Public disclosure of patent application 59-45944
43) Public disclosure March 15, 1984

51) Int. Cl.3	Identification symbol	Number of in-office registration
C 03 C 25/02		8017-4 G
C 03 B 37/00		6602-4 G
G 02 B 5/14		L 7370-2 H

Number of inventions 1
Requests for examination not yet
(8 pages in total)

54) Method of production of glass fibers for optical communication

21) Patent application	57-152240
22) Date of application	August 31, 1982
72) Inventor	.. MARUYAMA Technical division of Kansai Paint Co., Ltd. Hiratsuki-shi, Higashi-Yawata 4 chome 17-1
72) Inventor	Takao YAMAMOTO Technical division of Kansai Paint Co., Ltd. Hiratsuki-shi, Higashi-Yawata 4 chome 17-1
71) Applicant	Kansai Paint Co., Ltd. Amagasaki-shi, Kanzaki-cho 33-1
74) Agent	patent attorney Eiji SAIGUSA and 2 others

Specification.

Title of the invention.

Method of production of glass fibers for optical communication.

What is claimed.

(1) A method of production of a glass fiber for optical communication with the characteristic that a coating composition that is set by electron beams, with a glass transition temperature of the set coating material of -200°C or less or 700°C or more, is painted on the surface of the glass fiber for optical communication, and that the said coating composition that is set by electron beams, is set by irradiation with electron beams of 50 KeV to 500 KeV.

Detailed description of the invention.

This invention pertains to a method of production of a glass fiber for optical communication, and with more details, it pertains to a method of coating of the fiber for optical communication with a coating material.

In general, the material of glass fibers for optical communication that is made by spinning of an optical glass material such as quartz, has various characteristic features such as a small loss of transmission of light, a high flexibility and in addition a light weight. In recent years, attention has been paid to these characteristic features of the glass fibers, and they have come to be used in various kinds of communication cables, communication channels in buildings and communication circuits in cars etc.

In order to maintain flexibility, in general glass fibers for optical communication usually have a diameter of 200 micron or less. It is known that in the course of time, the strength of such glass fibers declines by the influence of humidity etc. Moreover, in the process of production of glass fibers, fine cracks are readily produced in the surface, and by these cracks, mechanical strength declines, and by adsorption of the humidity

in the air, water invades in the cracks, and they grow wider, and the mechanical properties have a tendency to further deterioration. Therefore, it is difficult to use glass fibers as such as the medium for optical communication, and as is well known, a coating is performed on glass fibers for optical communication.

In the method of coating of glass fibers for optical communication, various methods of setting of coating materials, such as the method of heating (patent disclosure 54-158942 (1979), patent disclosure 55-140741 (1980)) and the method of setting by ultraviolet rays, have been investigated, and it is said that among them, ultraviolet settable coating materials that have a number of advantages, are useful as a primary coating material, from the viewpoint of productivity of glass fibers for optical communication. As this method, for instance patent disclosure 54-42496 (1979) and patent disclosure 55-42246 (1980) can be mentioned. The spinning of glass fibers for optical communication is carried out with the use of heating sources such as a high frequency heating furnace, resistance heating furnace, oxygen-hydrogen flame, carbonic acid gas laser etc. As is carried out in patent disclosure 54-42496 (1979), the painting of the glass fiber is carried out by painting an ultraviolet setting resin composition immediately after the spinning of the fiber, before it touches another solid material, and fusing and drying it in the time wherein it reaches the winding machine. For complete fusion and drying, it was necessary that the distance from the spinning furnace to the winding machine is long, that a long drying furnace is installed, or that spinning is carried out with an extremely slow linear speed, and in order to raise productivity, an extremely big installation was necessary.

Moreover, for the control of the accuracy as a fiber for optical communication, a linear speed at or above a certain value is necessary in the spinning, and consequently, production at a high speed is necessary. As one of such methods, the method wherein the coating material is set by ultraviolet irradiation has been proposed in patent disclosure 54-42496 (1979).

For setting of photosetting resins by ultraviolet rays, however, the order of about 100 m/minute is the limit, and when a rise of productivity is wanted, the installation is large and running costs and maintenance costs rise to a high level.

The present inventors discovered a method of coating of glass

fibers for optical communication wherein the weak points of the existing methods have been eliminated, and a much better productivity than in the ultraviolet setting method is obtained, and they achieved the completion of this invention.

This invention pertains to a method of production of a glass fiber for optical communication with the characteristic that a coating composition that is set by electron beams, with a glass transition temperature of the set coating material of -200°C or less or 700°C or more, is painted on the surface of the glass fiber for optical communication, and that the said coating composition that is set by electron beams, is set by irradiation with electron beams of 50 KeV to 500 KeV.

In this invention, an electron beam setting coating composition with a glass transition temperature of the coating material after setting of -200°C or less or 700°C or higher, is used as the coating material of the glass fiber for optical communication.

Such electron beam setting coating compositions are obtained by mixing monomers for adjustment of the glass transition temperature and additives if necessary, with unsaturated polymers or unsaturated oligomers.

The unsaturated polymers that are used in this invention are coating forming resins that can crosslink and polymerise by irradiation with electron beams, viz., resins that can be polymerised and set by the energy of electron beams, wherein basic resins with saturated bonds as the skeleton, that have functional radicals, as is shown in table 1, and vinylic monomers (examples shown in table 2) that have radicals that can carry out an addition or condensation reaction with the said functional radicals, are reacted with the well known existing reaction methods, and as the basic resin, for instance one or two or more that are chosen from acrylic resins, polyester resins, epoxy resins, amino resins (for instance melamine resin), polyamide resins, polyurethane resins, vinyl resins, silicone resins, and dienic resins etc., can be mentioned, and examples of the functional radicals in the vinylic monomer that should be reacted with the various functional radicals that are present in these basic resins, are as shown in table 1. Moreover, concrete examples of vinylic monomers that have such functional radicals are as shown in table 2.

Moreover, the unsaturated oligomers are for instance compounds with 2-4 polymerisable vinyl radicals with a molecular weight of 1000 or less, and concrete examples thereof are diallylphthalate, ethyleneglycoldi(meth)acrylate, tetra-ethyleneglycoldi(meth)acrylate, bis-(ethyleneglycolphthalate)di(meth)acrylate, bis-(diethyleneglycolphthalate)di(meth)acrylate, polyethyleneglycoldi(meth)acrylate, polypropyleneglycoldi(meth)acrylate, trimethylolpropanetri(meth)acrylate, the product of the addition reaction of the 1:1 (molar ratio) adduct of trilenediisocyanate and hydroxyalkylester of (meth)acrylic acid, with trimethylolethane or trimethylolpropane, and mono- or die-ester compounds of polybasic acids such as pentaerythritoltetra(meth)acrylate, phthalic acidanhydride, adipic acid, succinic acid, and hexahydrophthalic acidanhydride, and hydroxyethylacrylate, hydroxypropylacrylate, hydroxyethylmethacrylate and hydroxypropylmethacrylate.

Such unsaturated polymers or oligomers preferably have 0.5 to 5 α, β -olefinic unsaturated bonds per 1000 g resin.

Table 1.

monomer polymerisable vinylic monomer that has a radical with addition or condensation reactivity with the following functional radical

functional radical in base resin	functional radical	concrete example of vinylic monomer
hydroxy radical	epoxy radical	(4) in table 2
	carboxylic acid-anhydride radical	(3) "
	carboxyl radical	(2) "
	isocyanate radical	(7) "
	methylol radical	(5) "
	alcoxymethylol radical	(6) "
carboxyl radical	epoxy radical	(4) "
	hydroxy radical	(1) "
	isocyanate radical	(7) "
	amino radical	(9) "
	aldehyde radical	acrolein croton aldehyde
carboxylic acid-anhydride radical	hydroxy radical	(1) in table 2
	methylol radical	(5) "
	epoxy radical	(4) "
	amino radical	(9) "
epoxy radical	hydroxy radical	(1) "
	carboxyl radical	(2) "
	carboxylic acid-anhydride radical	(3) "
	methylol radical	(5) "
	amino radical	(9) "
	chloro radical	(10) "

methylol radical	hydroxy radical	(1)	"
	isocyanate radical	(7)	"
	carboxylic acid-anhydride radical	(3)	"
	alcoxymethylol radical	(6)	"
	epoxy radical	(4)	"
	aldehyde radical	acrolein croton aldehyde	"
	chloro radical	(10) in table 2	"
alcoxymethylol radical	hydroxy radical	(1)	"
	methylol radical	(5)	"
isocyanate radical	hydroxy radical	(1)	"
	methylol radical	(5)	"
amide radical	chloro radical	(10)	"
	aldehyde radical	acrolein croton aldehyde	"
	amide radical	(8) in table 2	"
amino radical	epoxy radical	(4)	"
	carboxyl radical	(2)	"
	aldehyde radical	acrolein croton aldehyde	"
	carboxylic acid-anhydride radical	(3) in table 2	"
	chloro radical	(10)	"
	epoxy radical	(4)	"
chloro radical	methylol radical	(5)	"
	amide radical	(8)	"
	amino radical	(9)	"
	amino radical	(9)	"

Table 2.

functional radical	vinyllic monomer
(1) hydroxy radical	hydroxyethyl acrylate hydroxyethyl methacrylate hydroxypropyl acrylate hydroxypropyl methacrylate allyl alcohol
(2) carboxyl radical	acrylic acid methacrylic acid itaconic acid
(3) carboxylic acid-anhydride radical	maleic acid anhydride itaconic acid anhydride
(4) epoxy radical	glycidyl acrylate glycidyl methacrylate aryl glycidyl ether
(5) methylol radical	methylol acrylamide
(6) alcoxymethylol radical	alkyl (methyl, ethyl, isopropyl, butyl, amyl) ether compound of methylol acrylamide
(7) isocyanate radical	cyanoacrylate 1:1 (molar ratio) adduct of hydroxy radical containing vinyl monomer and di-isocyanate compound (for instance adduct of 1 mol hydroxyethyl methacrylate and 1 mol triene di-isocyanate)
(8) amide radical	acrylamide methacrylamide
(9) amino radical	aminoalkyl methacrylate aminoalkyl acrylate

(10) chloro radical

acrylic acid chloride
methacrylic acid chloride
vinylchloride
vinylidene chloride
hydrochloric acid adduct with epoxy
radical of glycidyl acrylate and
glycidyl methacrylate

As the unsaturated monomers that, as has been mentioned above, are combined with unsaturated polymers or oligomers, acrylic acid and esters thereof, methacrylic acid and esters thereof, aromatic vinyl monomers, vinylacetate and vinylether etc. can be used. As typical examples thereof, methylacrylate, ethylacrylate, propylacrylate, butylacrylate, ethylhexylacrylate, octylacrylate, decylacrylate, laurylacrylate, carbitolacrylate, methylmethacrylate, ethylmethacrylate, propylmethacrylate, butylmethacrylate, ethylhexylmethacrylate, octylmethacrylate, decylmethacrylate, laurylmethacrylate, carbitolmethacrylate, hydroxyethylacrylate, hydroxypropylacrylate, hydroxyethylmethacrylate, hydroxypropylmethacrylate, ether compounds of alkyleneoxides such as ethyleneoxide, propyleneoxide and butylene oxide, and hydroxyethylacrylate, hydroxypropylacrylate hydroxyethylmethacrylate and hydroxypropylmethacrylate, and acrylic acid, methacrylic acid, styrene and vinyltoluene etc. can be mentioned.

The electron beam settable coating composition of this invention is obtained by mixing of the unsaturated polymers and oligomers and unsaturated monomers as have been mentioned above, and proper mixing thereof so that the desired glass transition temperature is obtained. Polymers that give a glass transition temperature of -200 C or less, can be properly chosen from polybutadienic, acrylic, urethane, and modified polyester systems, and on the other hand, polymers that give a glass transition temperature of 700 C or higher, are in general chosen from acrylic, polyester, epoxy and silicone systems etc. Moreover, by admixture of unsaturated oligomers with 2, 3 or 4 functions, the effect is obtained that the cross linking density is increased and that the glass transition temperature is raised.

In the electron beam settable coating composition that is used in this invention, additives such as pigments, dyes and fillers, that are usually used in paints, can be mixed, if wanted, in addition to the above mentioned indispensable components.

As has been discussed above, an electron beam settable coat-

ing composition with a glass transition temperature after setting of 700 C or higher or -200 C or less can be obtained in a simple way by mixing unsaturated monomers and, if wanted, mixing additives, with unsaturated polymers or unsaturated oligomers. In the production of fibers for optical communication by applying the thus obtained coating composition on the glass fiber for optical communication and setting, for instance a production installation as is shown in figures 1-3, is used. In these figures 1, 7 and 14 are spinning furnaces with high frequency heating, 2, 8 and 15 are glass fibers that have been spun, 3, 9 and 16 are installations for coating of the electron beam settable coating composition, 4, 10 and 17 are electron beam irradiating installations, 11 is an after-heating device, 18 is an ultraviolet irradiating device, 5, 12 and 19 are guide rollers and 6, 13 and 20 are winding machines.

In the application of the electron beam settable coating composition on the surface of the spun glass fiber, it is useful if the thickness of the applied film of the coating composition whereof the glass transition temperature of the coating film after setting is -200 C or less, usually is 10-200 microns, and on the other hand, it is usually 5-50 microns in the case that the glass transition temperature is 700 C or higher. In the former case, deterioration of water resistance of the coating film accelerates when the film thickness is less than 10 microns, and the transparency for electron beams deteriorates if it exceeds 200 microns. In the latter case, water resistance deteriorates when the film thickness is less than 5 microns, and flexibility of the coating film deteriorates if it exceeds 50 microns.

For fibers for optical communication, it is necessary that, in the temperature range wherein it is usually used, the specific volume of the coating material actually does not change, and when the specific volume changes, the effect is that fiber for optical communication produces microbendings, and that the transmission loss of light increases. In fibers for optical communication whereon the electron beam settable coating composition of this invention, with a glass transition temperature of the set coating material of -200 C or less or 700 C or higher, has been applied, however, changes of the specific volume of the coating material in the temperature range wherein it is usually used actually does not occur, and consequently, defects as have

been mentioned above do absolutely not occur.

Accelerators of the electron beam generating source that is used in the electron beam irradiation after application of the electron beam settable coating composition, are for instance the Cockroft type, Cockroft-Walton type, Van de Graaff type, resonance transformer type, transformer type, insulated core transformer type, dynamitron type, linear filament type, and high frequency type etc. The proper range of the energy of the electron beam whereby the applied film of the electron beam settable coating composition of this invention is set and dried, is 50 KeV to 500 KeV, and preferably 100 KeV to 300 KeV. A proper quantity of irradiation is 0.2 Mrad to 15 Mrad, and preferably 1 Mrad to 5 Mrad. In the case that the quantity of irradiation is less than 0.2 Mrad, the setting of the coating material is not complete, and a sufficient performance of the applied film is not obtained. Moreover, if the quantity of irradiation exceeds 15 Mrad, this also exerts an influence on the glass fiber, and has the risk that a deterioration of mechanical strength is brought about.

In the case that electron beams are radiated on a wide object, it is necessary to spread the electron beam homogeneously in the lateral direction, and typical methods therefore are the usual scanning method and linear filament method (American patent 4246297). With both methods, ones with a width in the order of ca. 1 m are actually used in general for the setting of the coating material. Because the basic material of the glass fiber for optical communication in itself is very fine (200 microns or less), a length of the electron beam irradiation of several microns to several tens of microns in the lateral direction is sufficient. In case of the linear filament type, a more effective, high running speed is obtained, and also productivity can be greatly improved, if the fiber of the device for application of the electron beam setting coating composition is vibrated in the direction that is parallel to the filament.

Because electron beam setting occurs instantly, stress is readily produced in the painted film, and in such cases, the stress is mitigated by after-heating by the method that is shown in figure 2. Moreover, in some cases colouration occurs when glass is irradiated by a large quantity of electron beams. In such cases, in general the colouration is eliminated by diving

heating energy or light energy by the method that is shown in figure 2 and figure 3.

According to the method of this invention, a speed of setting and drying by electron beams of 150 m/min to 900 m/min in a length of ca. 1 m of the electron beam irradiated section is obtained, and productivity is remarkably improved, and the obtained coating material has an extremely good volume stability, and glass fibers for optical communication with excellent properties are obtained.

Below, further details of this invention are described by examples of execution. Herein, 'parts' means 'wt parts'.

Example of execution 1.

A coating preparation that consists of 100 parts acrylated polybutadiene (degree of polymerisation 1000), 20 parts 2-ethylhexylacrylate, and 0.1 parts silicone additive, was applied (painted) on a glass fiber (diameter 120 μ), that had been obtained by heating the mother material at ca. 20000 C, and pulling with a speed of 200 m/min, to obtain a coating material of 50 μ . Thereafter, the coating material was electron beam irradiated by a scanning type of electron beam accelerator with a speed of 200 m/min in the direction that is parallel to the scanning direction, under the conditions of an electron beam energy of 300 KV and an electronbeam current of 30 mA. The scanning width was 60 cm, and the width of the electron beam was ca. 3 cm. The glass transition temperature of the obtained coating material was -480 C. The film thickness of the optical fiber that had been coated in the painting device (device for application) was 50 μ , and its average breaking strength was 400 kg/mm². This coated fiber was immersed during 30 days in water at room temperature, and thereafter, the breaking strength was 380 kg/mm².

Example of execution 2.

An unsaturated acrylic resin with a molecular weight of 8000 was obtained by copolymerisation of 60 parts n-butylacrylate, 35 parts ethylacrylate, and 5 parts glycidylacrylate at room temperature, and adding thereafter again 10 parts acrylic acid. By addition and mixing of 20 parts Aronix M-113 (trade name of 4-nonylphenoxypolyethoxyacrylate. Toa Gosei Co.). and 2 parts tri-

methyloolpropanetriacrylate in 100 parts of this resin, an electron beam settable type of coating preparation was obtained.

The above mentioned coating preparation was applied on a glass fiber (diameter 100 μ) of the quartz type, that had been heated and drawn at 20000 C, to obtain (a thickness of) 100 μ , and by an electron beam accelerator of the scanning type, electron beam irradiation of the coating material of the painting device was carried out in an atmosphere of an inert gas with a speed of 300 m/min with an electron beam energy of 260 KV, an electron beam current of 40 mA, and a scanning width of 90 cm, in the direction that is parallel to the scanning direction.

Thereafter, the glass fiber whereon this coating had been applied was exposed during 2 seconds to an atmosphere of 2000 C. The glass transition temperature of this coated and set material was -250 C.

The water resistance and boiling water resistance of the coated glass fiber were good.

Example of execution 3.

An electron beam setting coating preparation that consisted of 10 parts carbitolacrylate, 2 parts hexanedioldiacrylate and 1 part silicone additive L-7001 (product of Nippon Unitika Co., Ltd.) in 100 parts polyether urethaneacrylate resin (molecular weight 2000, 2 terminal unsaturated acrylate radicals/1 molecule) was obtained.

The above mentioned coating preparation was applied on a glass fiber (diameter 90 μ) that had been obtained by heating the mother material to 20000 C and drawing, to obtain a thickness of 20 μ , and by an electron beam accelerator of the linear filament type, electron beam irradiation was carried out in an atmosphere of an inert gas, with the coating material flowing in the direction that is parallel with the filament. The irradiation width of the electron beam in the direction that is parallel to the filament was 60 cm, and the electron beam energy was 200 KV, and the electron beam current was 25 mA. The radiation speed of the electron beam in this case was 250 m/min. Thereafter it was after-heated during 1 second in an atmosphere of 2800 C. The glass transition temperature of this set coating material was -300 C, and the strength and water resistance of the obtained glass fiber were good.

Example of execution 4.

An electron beam settable coating material that consisted of 100 parts unsaturated acrylic resin (one wherein HEA had been introduced by an urethane reaction and unsaturated radicals had been introduced in 2 EHA, iBa, HEMA copolymer by an urethane reaction) (molecular weight 3000, a total of 1.5 double bonds per 1000 molecular weight) 20 parts Toray Thiokol LP-3 (trade name polysulfide polymer, product of Toray Thiokol Co.), 10 parts Aronix 5500 (Product of Toa Gosei Co.), 5 parts reactive diluant QM 672 (product of Rohm and Haas), and 0.5 parts additive (BYK 301, product of BYK Mallinckrodt Co.), was obtained.

A mother material with quartz glass as the main body, was heated to 20000 C, and a glass fiber was spun, and immediately thereafter, the above mentioned paint was applied to obtain 50 μ , and by a linear filament type of electron beam accelerator, this was irradiated with electron beams with an electron beam radiation speed of 400 m/min, in the direction that is parallel to the filament.

Thereafter, it was irradiated during 0.5 sec with an ultra-violet lamp of 20 KW. The glass transition temperature of this set coating material was -290 C.

The breaking strength and water resistance of the coated glass fiber were good.

Example of execution 5.

An electron beam setting paint that consisted of 100 parts epoxy acrylate resin (molecular weight 600), 20 parts hexanediol-diacrylate, 5 parts trimethylol (trimethylol ? translator) propane triacrylate, and 1 part silicone additive, was obtained.

The above mentioned coating material was painted on a glass fiber (diameter 100 μ) with quartz glass as the main component, immediately after spinning, to obtain 30 μ , and by an electron beam accelerator of the linear filament type, this was irradiated with an electron beam with a radiating speed of 500 m/min.

The glass transition temperature of the obtained coating material was 820 C, and the breaking strength and water resistance of the obtained glass fiber were good.

Example of execution 6.

An electron beam settable paint that consisted of 100 parts

urethane acrylate resin (molecular weight 700), 20 parts pentaerythritol triacrylate, 20 parts neopentylglycol diacrylate and 1 part additive, was obtained.

A glass fiber with quartz glass as the main component was spun by heating a mother material to 20000 C, and immediately thereafter, the above mentioned paint was applied to obtain 50 μ , and by an electron beam accelerator of the scanning type, electron beams were radiated in two cycles with a radiation speed of 250 m/min.

Thereafter, it was exposed 1 second in an atmosphere of 3000 C, and a coated glass fiber was obtained. The glass transition temperature of this coating material was 1050 C.

The water resistance and breaking strength of the obtained glass fiber were good.

Brief description of the figures.

Figure 1, figure 2 and figure 3 are schematic drawings of the installations for production of glass fibers for optical communication that are used in this invention.

The agent, patent attorney Eiji SAIGUSA